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The Metal Complexes of Tris-Anhydro Ortho-Aminobenzaldehyde: I. Metal Ion Catalysis of the Trimerization of Ortho-Amino-Benzaldehyde. II. The Stabilization of Low Oxidation States by Coordination.

Rashid Abdul Latif

Louisiana State University and Agricultural & Mechanical College

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THE METAL COMPLEXES OF
TRIS-ANHYDRO-ORTHO-AMINOBENZALDEHYDE

- I. METAL ION CATALYSIS OF THE TRIMERIZATION
OF ORTHO-AMINOBENZALDEHYDE
- II. THE STABILIZATION OF LOW OXIDATION STATES
BY COORDINATION

A. Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Rashid Abdul Latif
B. S., Higher Teachers College (Baghdad, Iraq) 1943
M. A., University of Texas, 1949
June, 1953

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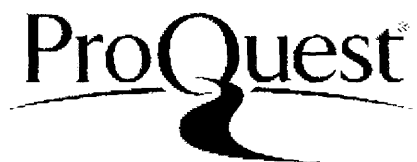


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ABSTRACT

In a reaction analogous to the conversion of phthalonitrile to phthalocyanine, copper (II), nickel, and cobalt (II) ions react with ortho-aminobenzaldehyde to produce complexes of a trimeric condensate, tris-anhydro-ortho-aminobenzaldehyde. This quadridentate coordinating agent is also formed by treatment with manganous salt, but in this instance the isolated compound contains no complexed metal ion.

Tris-anhydro-ortho-aminobenzaldehyde exhibits a remarkable ability to stabilize low oxidation states, bringing about the reduction of copper (II) to copper (I), and preventing the oxidation of cobalt to the +3 state. The copper (I) complex may be oxidized under favorable conditions, such as high pH, and it may undergo disproportionation in the presence of suitable agents, such as mercury and halide ion.

I. INTRODUCTION

The end of the nineteenth century witnessed the formulation of many of the chemical generalizations, whose further development and application have occupied the minds of chemists in the present century. Among the ideas promulgated at that time was Werner's coordination theory, the immediate objective of which was the interpretation of the structure of the "addition compounds" of metal salts with other molecules, which already satisfied the usual valence requirements of all their atoms. During the period following Werner's pronouncement of his theory, a great deal of attention was focused upon the study of complex inorganic compounds that resulted from simple "addition" of metal salts to other molecules.

During the last twenty years the study of coordination compounds has undergone considerable change in emphasis. One characteristic of this transition has been the shift from qualitative, descriptive studies to the determination of the behavior of complexes from a physical chemical point of view. A second feature of recent developments in this field has been the recognition that complex formation does not necessarily occur by a simple additive process involving the components of the complex, but that indeed extensive modifications may occur in the donor and acceptor molecules as a result of coordination. Our understanding of these

modifications is of utmost importance in the elucidation of the mechanism of the catalytic behavior of metal ions in numerous chemical reactions, including the enzymatic reactions characteristic of physiological processes.

The present investigation represents a study of a complexation reaction between a variety of metal ions and ortho-amino-benzaldehyde. In all of these reactions the metal ion exerts a profound influence upon the organic molecule, bringing about trimerization of the bidentate amino-aldehyde to a quadridentate compound. In one instance, the reaction with copper ion, the organic molecule has an effect of comparable magnitude on the metal ion, causing it to change its oxidation state.

The driving force for the changes that occur in donor and acceptor during a coordination reaction is provided by the great stability of the resulting complex. Only when simple addition alone is capable of the production of a stable complex does coordination proceed without modifications in the components of the reaction.

II. HISTORICAL

A. Condensation Reactions Catalyzed by Metal Ions.

One of the most interesting and useful applications of coordination compounds is based upon the ability of metal ions to bring about the condensation of organic molecules to form complexes of definite composition. Sometimes such condensation occurs only in the presence of metal ions, in other instances condensation may be achieved with or without the metal, but the latter enhances either the rate or the yield of the reaction. Occasionally the effect of the metal ion is to direct the condensation to the formation of a single product, and to avoid the production of a mixture of substances of varying molecular dimension.

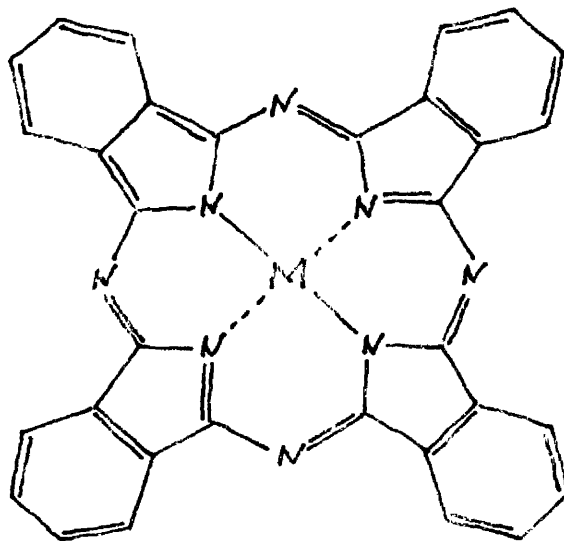
As a result of these catalytic condensations chelates of the metal ion and the condensed organic molecule generally are formed, and sometimes precipitate from solution.

Organic molecules containing three or more coordinating donors may give rise to multiple ring chelate structures; they are called tri- and quadridentate molecules. A tridentate structure, analogous to the condensed rings of naphthalene, is exemplified by the metallic complexes of diethylene triamine; an illustration of a quadridentate system is offered by the complexes of acetyl acetone-ethylenediamine.(1)

A classic example of a metal catalyzed condensation to a quadridentate system is the formation of the phthalocyanine complexes from phthalonitrile. The first of these compounds was discovered accidentally, through analysis of traces of a dark blue substance formed in molten phthalimide during its preparation from phthalic anhydride and ammonia in iron vessels (2). Further studies led to the conclusion that the phthalocyanine was formed by a process of dehydration to the phthalonitrile, which, in turn, condensed to form the iron phthalocyanine complex.

Byrne, Linstead, and Lowe (3) then prepared the magnesium, nickel, manganese, and copper phthalocyanine derivatives directly from phthalonitrile.

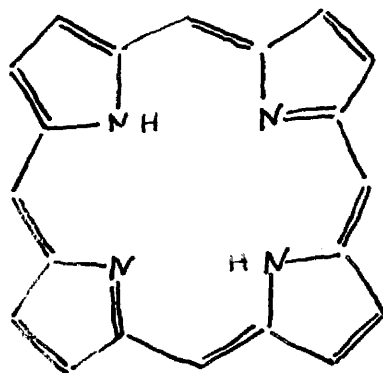
The structure of phthalocyanine has been studied by Dent, Linstead, and Lowe (4); and from a series of experiments it was concluded that the metal was held by coordinate covalent bonds to four nitrogen atoms, suggesting the following structure for the complex:



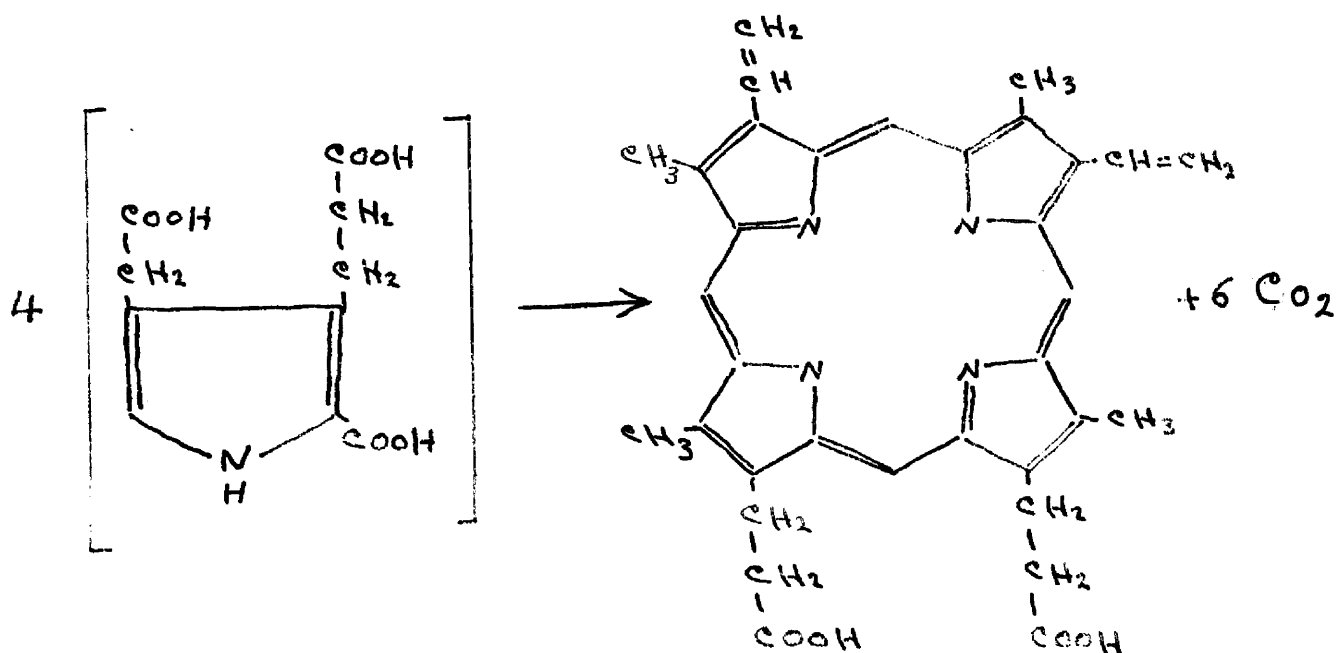
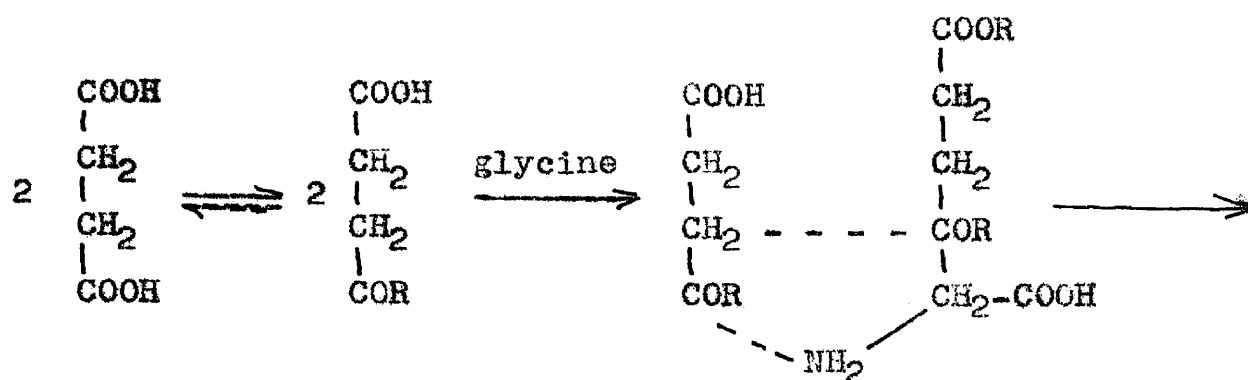
This structure has now been fully confirmed by X-ray analysis (5).

Copper phthalocyanine is exceedingly stable; it is not affected by molten alkali or boiling hydrochloric acid. It can be purified by sublimation in vacuum (500°) or by dissolving in concentrated sulfuric acid, from which it is recovered by dilution. It is completely insoluble in all the usual organic solvents.

The biologically important porphyrins bear a remarkable similarity to the synthetically produced phthalocyanines. The parent compound of the porphyrins, porphine, has the following structure:



The porphyrins themselves contain organic radicals substituted in the β - positions of the pyrrole rings; the metal in chlorophyll is magnesium, whereas the heme porphyrins of hemoglobin and the respiratory enzymes contain iron. The following mechanism has been postulated for the physiological synthesis of the porphyrin molecule, on the basis of studies with labelled carbon atoms (6):



It appears highly probable, in view of our knowledge of the process of phthalocyanine formation, that complexation is responsible for the condensation of succinic acid with glycine to produce the porphyrin. The metal ion for complex formation may well be furnished by a metal enzyme system.

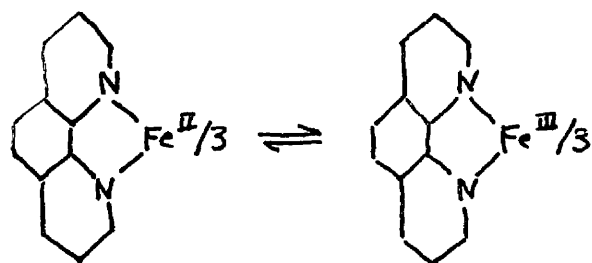
B. Stabilization of Low Oxidation State by Coordination.

1. General Principles.

A variety of factors are responsible for bringing about the stabilization of either the higher or the lower oxidation state of a metal ion through complex formation. These factors will be discussed presently from the point of view of low oxidation state stabilization, since this phenomenon is involved in the experimental portion of this thesis.

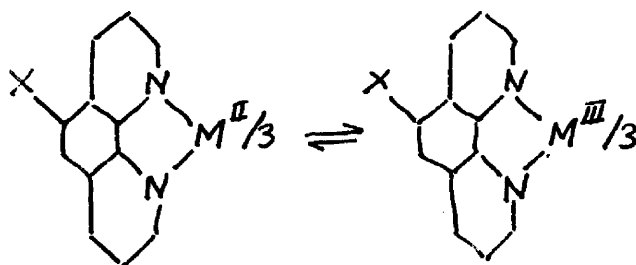
Chemical and physical changes tend to bring about an increase in the entropy of the universe; any system in a given state is more stable when the entropy change toward any other state is accompanied by an entropy decrease. Ionization generally decreases the entropy of the solvent because it restricts the degree of freedom of the solvent molecules in the vicinity of the ions; furthermore, the higher the charge of the ions, the greater will be the entropy decrease and the lower the stability of the ions. According to this principle, therefore, the entropy effect tends to stabilize cations in their lower oxidation states(7).

The electronic structure is another factor which can influence the degree of stability of a particular oxidation state of a metal. In the couple ferro-ferri-o-phenanthroline,



the ferrous chelate is more stable than the ferric chelate, because in the ferrous form the 3d, 4s, and 4p orbitals are filled completely, giving it the xenon electronic structure, while in the ferric form one electron in the 3d orbital remains unpaired.

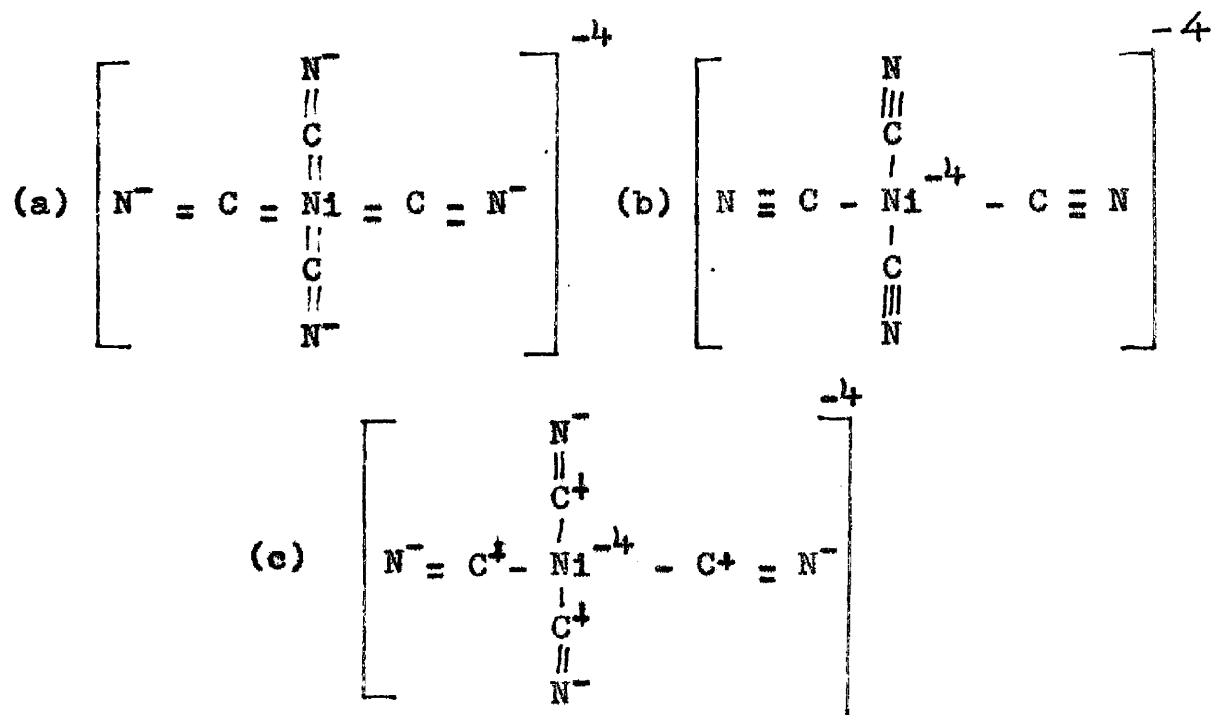
The donor power of the chelating group is a third factor governing the stability of a certain oxidation state of a metal. The substituted o-phenanthroline metal chelate is an example of how such stability can be altered by changing the substituted group. In the system,



if the (x) is an electrophilic group, the electron density about the metal (M) will decrease and consequently the metal will carry the higher oxidation state, while if (x) is a nucleophilic group, the electron density about the metal will increase, forcing the metal to accept an electron and converting it to the lower oxidation state (8).

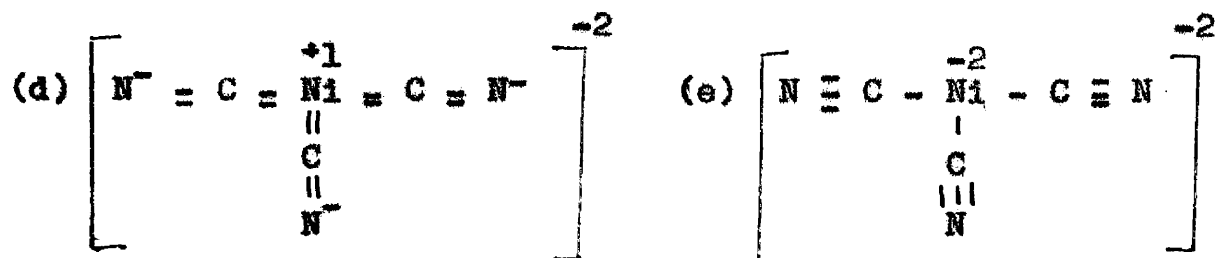
The lower oxidation states of metals are formed by coordination reactions that take place in reducing solvents. Chromium (II) halides (with the exception of the fluoride) and sulfate are stable in hydrazine. $\text{CrCl}_2 \cdot 2\text{N}_2\text{H}_4$ is stable in air for days (9), and a number of chromium (II) salts are

not even oxidized when suspended for a long time in water in contact with air. Eastes and Burgess (10) discovered that the product of the reaction between an excess of alkali metal in anhydrous liquid ammonia with alkali metal cyanonickelate is not the nickel metal, as had been anticipated, but rather a compound having the empirical formula $M_4Ni(CN)_4$, where (M) is an alkali metal. Deasy (11) has accounted for the stabilization of such an unusual oxidation state of nickel in this compound by postulating the existence of the following resonance hybrid:



The contribution of structure (a) is probably greater than the contributions of the other two structures, since it does not confer a negative charge upon the metal atom.

When, on the other hand, an excess of alkali metal cyanonickelate was allowed to react with alkali metal in anhydrous liquid ammonia, a compound of empirical formula $M_2Ni(CN)_3$ was formed in which nickel appears to be monovalent; the following resonance structures were assigned to account for this compound:



Structure (d) was considered more important, because it involves a positive dipole on the nickel atom.

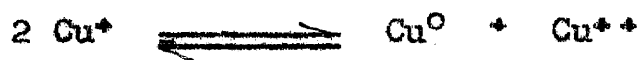
Palladium was found to behave in a way similar to nickel in these reactions (12). Treatment of alkali metal in anhydrous liquid ammonia with potassium tetracyanopalladate (II) resulted in the formation of potassium tetracyanopalladate (0), which was found to be more soluble and less stable than the corresponding nickel complex.

2. Copper (I).

Copper forms compounds in which its oxidation state is +1, +2, and +3. The most stable of these in aqueous solution is the +2 state, but it is possible to bring about reduction to the +1 state in the presence of various precipitating and

complexing agents. Tripositive copper exists only in the presence of powerful oxidizing agents, and it is very unstable.

The stable copper (I) salts have been considered to be those in which the copper possesses a considerable degree of covalent character and the stability of these complexes appears to be a function of covalent character (13). The increase in stability of the copper (I) halides from fluorine to iodine is evidence for the above hypothesis. Furthermore, it has been found that with decrease in dielectric constant of the solvent, there is a displacement of the equilibrium

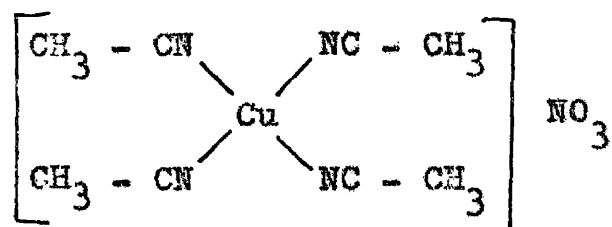


in such a direction as to favor the copper (I) state (14).

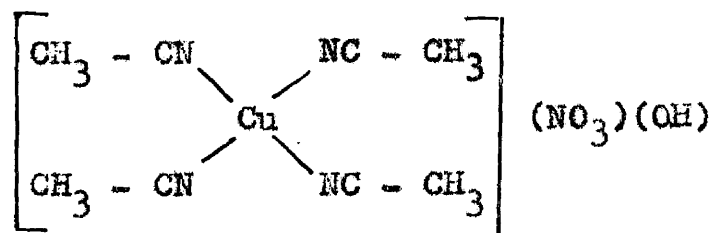
Various coordinating agents, such as chloride ion, ammonia, and most amines, form in aqueous solution stable copper compounds containing copper in the +1 state. Methylamine, pyridine, and pentamethylenediamine produce complexes with copper in the +1 state, while ethylenediamine and trimethylenediamine favor the +2 state. No explanation has been given to account for this difference.

Among other coordinating agents which stabilize the copper (I) state are the aceto- and succinonitrile, thiourea (tu) and ethylenethiourea (etu), and phosphine and arsine.

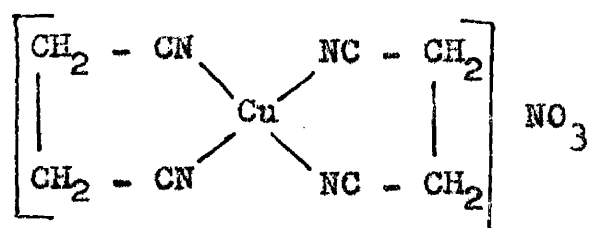
Morgan (15) has reported that on the addition of finely divided copper to a dilute solution of silver nitrate in acetonitrile, and subsequent distillation of the mixture under an inert gas atmosphere, there remains a colorless crystalline substance, whose composition and structure suggest the following formula:



This substance was found to be stable in air for several hours; longer standing results in conversion to the copper (II) complex:

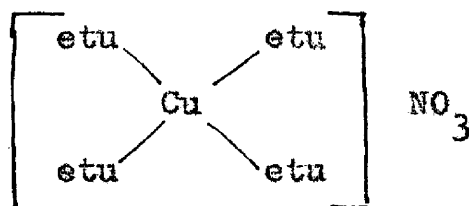


Succinonitrile, when used in place of acetonitrile, yields the following compound



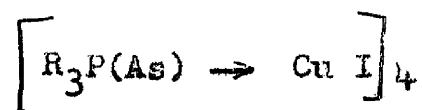
whose stability in air and conversion to the $+2$ complex resembles the corresponding behavior of the complex with acetonitrile.

Thiourea and ethylenethiourea were found to stabilize the copper (I) state (16). On mixing a hot aqueous solution of copper (II) nitrate and ethylenethiourea, a green color developed, which rapidly faded to produce a colorless liquid layer over the precipitated sulfur. After concentration and cooling of the colorless liquid, colorless crystals were formed whose structure may be represented by the following formula:



The copper is coordinated to the sulfur atom.

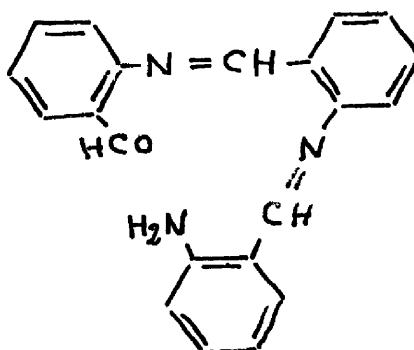
Mann, Purdie, and Wells (17) prepared copper complexes of the organic derivatives of phosphine (R_3P) and arsine (R_3As) in a solution containing excess potassium iodide; the white, non-ionic derivatives that resulted conformed to a structure involving the metal ion in the $+1$ state:



C. The Trimerization of Ortho-aminobenzaldehyde.

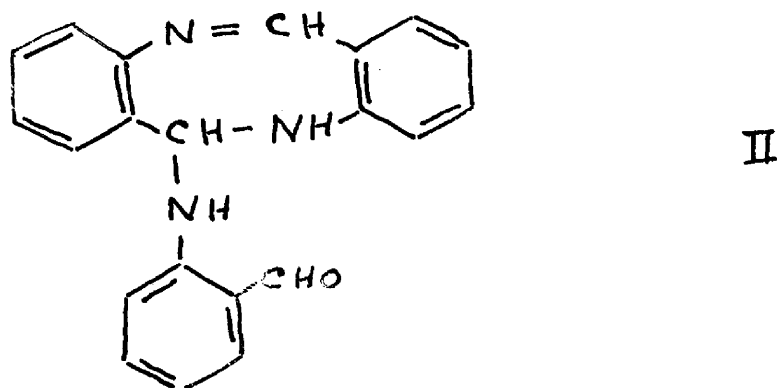
The chemistry of ortho-aminobenzaldehyde may be expected to be complicated by the fact that the molecule contains two functional groups, the amino and aldehyde groups, which are capable of reacting with each other. As a result of the present investigation it has been possible to determine under what conditions of complex formation such condensations are favored or avoided. It is of some importance, therefore, to understand the circumstances that have, in the past, led to condensation reactions of the amino-aldehyde.

It was discovered in 1926 by F. Seidel (18) that ortho-aminobenzaldehyde reacts with zinc chloride in anhydrous ether medium to produce a compound of empirical composition $C_7H_5N \cdot 1/2 ZnCl_2$, with a melting point of 348-350°C. Repeated recrystallization from glacial acetic acid led to the isolation of the tris-anhydro-ortho-aminobenzaldehyde, with a melting point of 235°. The following structure was assigned to the molecule:



and partly substantiated by the fact that treatment with acetic anhydride results in the formation of the monoacetyl derivative, indicating the presence of only one amino nitrogen.

A compound exhibiting the same physical properties as the one reported by Seidel was obtained by Bamberger (19) by allowing the amino aldehyde to remain in contact with water for four days. Bamberger speculated that the formula of the trimer may be the following:

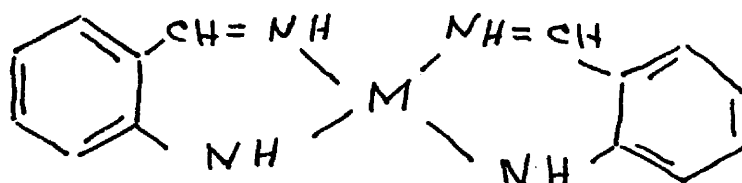


Seidel and Dick (20) obtained confirmatory evidence for structure II from the observation that two nitroso groups could be introduced into the molecule, thus displacing two hydrogen atoms of the secondary amino groups. Nitrosation of the monoacetyl derivative, in which one hydrogen had presumably been already displaced, yielded the mono-nitroso compound.

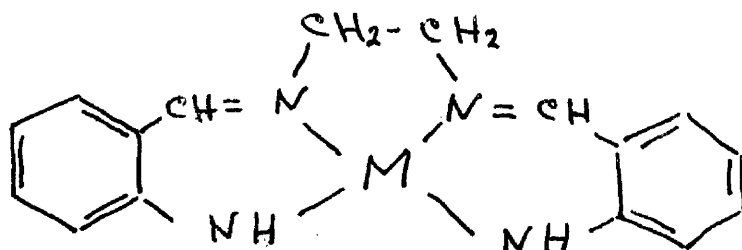
The trimeric condensation product can be obtained from the action upon the monomer of a variety of agents, such as phosphorus (V) oxide, hydrochloric acid, glacial acetic acid, etc. It must be emphasized that, in the solid state, this compound is relatively stable, 6 grams of monomer yielding only 0.1 gram of the trimer after six months' standing.

Experiments confirming the presence of one aldehyde group in the trimer (in either structure I or II) were the reactions with para-nitro-aniline and hydroxylamine; one mole of each condenses with one mole of the aldehyde trimer.

Metallic complexes involving derivatives of ortho-aminobenzaldehyde have been reported by Pfeiffer, Hasse, Pfitzner, Scholl and Thielert (21). The latter obtained the copper and nickel complexes of ortho-amino-benzaldimine by reaction of this compound with the metal sulfates dissolved in concentrated aqueous ammonia. The structures of these complexes were depicted thus:

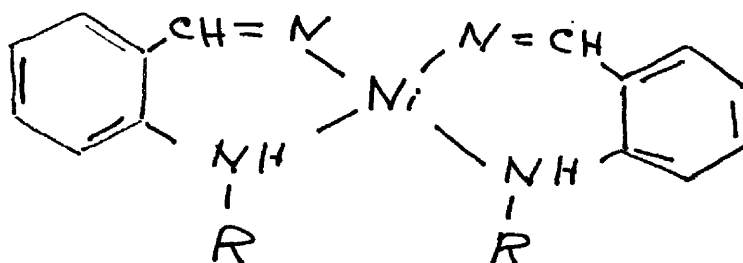


These same investigators were also able to isolate the Schiff's base of ortho-amino-benzaldehyde and ethylenediamine; the colorless compound melted at 178° . Reaction of an alcoholic solution of the Schiff's base with aqueous ammonia solutions of copper and nickel sulfate yielded complexes of the following composition:

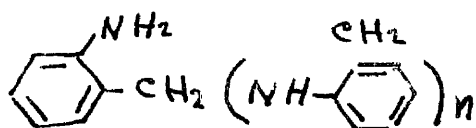


The copper complex was red brown, while the color of the nickel complex was dark red.

An unexpected preparation of Pfeiffer's nickel ortho-amino-benzaldimine complex came as a consequence of the catalytic hydrogenation of ortho-amino benzonitrile using Raney nickel in the presence of aqueous ammonia(22). In addition, indirect evidence indicated the presence in the reaction mixture of a second nickel complex, to which the following structure was ascribed:



R being



III. EXPERIMENTAL

A. Preparation of Ortho-aminobenzaldehyde.

This compound was prepared by the reduction of o-nitrobenzaldehyde with ferrous sulfate and ammonium hydroxide according to the directions given in Organic Syntheses (23). M. P. 39°-40°.

B. Reaction of Ortho-aminobenzaldehyde with Metal Ions.

1. Preparation of the Copper Complex of Tris-anhydro-ortho-aminobenzaldehyde.

A 200 ml. three necked round bottom flask was mounted on a steam bath and fitted with mechanical stirrer, reflux condenser, and 50 ml. separatory funnel. 3.63 grams (0.03 mole) of ortho-aminobenzaldehyde dissolved in 50 ml. absolute ethyl alcohol were introduced into the reaction flask and 2.41 grams (0.01 mole) of copper (II) nitrate trihydrate dissolved in 50 ml. absolute ethyl alcohol were poured into the separatory funnel. Stirring was initiated and the copper nitrate solution was added dropwise to the refluxing contents of the flask.

During the course of heating the color of the reaction mixture changed from yellowish blue through yellowish green to the deep olive green of the reaction product.

After refluxing for six hours, the mixture was transferred into a 100 ml. Erlenmeyer flask and heated on a steam bath until the volume had been reduced to approximately 20 ml. and a dark green crystalline precipitate had formed. The mixture was then cooled and filtered through a fritted glass funnel. The precipitate was washed five times with absolute ethyl alcohol and ether, and allowed to dry at 25°C. for 24 hours. M. P. $> 300^{\circ}\text{C}$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{N}_4\text{O}_4\text{Cu}$: C, 55.68; H, 3.78; N, 12.37.

Found: C, 55.28; H, 3.31; N, 12.72.

2. Preparation of the Nickel Complex of Tris-anhydro-ortho-aminobenzaldehyde.

The reaction assembly described above for the preparation of the copper complex of tris-anhydro-ortho-aminobenzaldehyde was also employed here.

3.63 grams (0.03 mole) of ortho-aminobenzaldehyde dissolved in 50 ml. absolute ethyl alcohol and 2.91 grams (0.01 mole) of nickel (II) nitrate hexahydrate in 50 ml. of absolute ethyl alcohol were mixed according to the procedure given in the above preparation. The color of the reaction mixture changed from light greenish to yellowish after one hour of refluxing. At the end of the preparation, which took eight hours, an orange crystalline precipitate had formed. This precipitate was washed and dried according to the above procedure. M. P. $> 300^{\circ}\text{C}$.

Anal. Calcd. for $C_{21}H_{17}N_5O_7Ni$: C, 49.44; H, 3.36; N, 13.73.

Found: C, 51.63; H, 3.24; N, 13.82.

3. Preparation of the Cobalt Complex of Tris-anhydro-ortho-aminobenzaldehyde.

3.63 grams (0.03 mole) of ortho-aminobenzaldehyde in 50 ml. of absolute ethyl alcohol and 2.91 grams (0.01 mole) of cobalt (II) nitrate hexahydrate in 50 ml. absolute ethyl alcohol were mixed according to the above procedure. The refluxing was continued for twelve hours, during which the color of the mixture changed from pinkish to yellowish brown. The solution was then transferred to an Erlenmeyer flask and concentrated on a steam bath, but no precipitate had formed after the volume of the mixture had been reduced to 20 ml. The solution was cooled, and distilled water was added gradually; a brown precipitate formed after the addition of few milliliters of water. The addition of water was continued until no further precipitation was evident. The precipitate was then filtered, washed a few times with distilled water, redissolved in alcohol, and reprecipitated with water. Finally it was filtered off and dried in a vacuum desiccator at $25^{\circ}C$. for 24 hours. M. P. $> 300^{\circ}C$.

Anal. Calcd. for $C_{21}H_{17}N_5O_7Co$: C, 49.42; H, 3.36; N, 13.72.

Found: C, 50.21; H, 3.77; N, 13.92.

4. Trimerization of Ortho-aminobenzaldehyde by the Action of Manganese (II) Ion.

3.63 grams (0.03 mole) of ortho-aminobenzaldehyde dissolved in 50 ml. absolute ethyl alcohol and 2.87 grams (0.01 mole) of manganese (II) nitrate hexahydrate in 50 ml. absolute ethyl alcohol were mixed and treated according to the procedure followed for the preparation of the cobalt complex of tris-anhydro-ortho-aminobenzaldehyde. A light yellowish precipitate was formed after the addition of water to the cooled alcoholic solution mixture. The precipitate was filtered and washed with water; it was then redissolved and reprecipitated several times, and finally filtered off and dried in a vacuum desiccator for 24 hours at 25°C. M. P. 138°-140°C.

Anal. Calcd. for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.24; N, 12.48. Found: C, 77.20; H, 5.42; N, 11.58.

C. Comparison of Some Physical and Chemical Properties of Monomeric and Trimeric Ortho-aminobenzaldehyde.

Monomeric ortho-aminobenzaldehyde (C_7H_7NO) is a slightly yellow compound; it melts at 39°-40°C. and decomposes before boiling. It is very soluble in alcohol, ether, acetone, and aniline. It is slightly soluble in chloroform, carbon tetrachloride, and benzene; and very slightly soluble in water. It reacts with concentrated mineral acids with

the evolution of a gas and the formation of an orange solution. The addition of dilute acids changes the color of the organic compound to pink without dissolving it, but further addition of concentrated acid ultimately brings about solution. No reaction was observed with ammonium hydroxide and with alkali in the cold.

The trimeric ortho-aminobenzaldehyde ($C_{21}H_{17}N_3O$) is also yellow and melts at 138° - $140^{\circ}C$. It is very soluble in alcohol, acetone, chloroform, aniline, and benzene. It is slightly soluble in ether and carbon tetrachloride, and insoluble in water. Its behavior toward mineral acids, ammonium hydroxide, and alkali resembles that of the monomer in every respect.

D. Physical Properties of the Copper, Nickel, and Cobalt Complexes of Tris-anhydro-ortho-aminobenzaldehyde.

1. Color and Solubilities.

The solubilities of the copper, nickel, and cobalt complexes of the tris-anhydro-ortho-aminobenzaldehyde in several solvents were determined qualitatively; the results are summarized in table 1.

Table 1

Color and Solubilities of Cu, Ni, and Co Complexes of
Tris-anhydro-ortho Aminobenzaldehyde

Complexes	Cu-Complex	Ni-Complex	Cobalt-Complex
Color	olive green	orange	brown
Solubilities in			
1. water	soluble	very soluble	insoluble
2. ethyl alcohol	soluble	insoluble	soluble
3. acetone	insoluble	insoluble	slightly soluble
4. ether	insoluble	insoluble	slightly soluble
5. chloroform	insoluble	insoluble	very slightly soluble
6. carbon tet	insoluble	insoluble	very slightly soluble
7. aniline	soluble	soluble	soluble
8. benzene	insoluble	insoluble	insoluble

2. Absorption Spectra.

0.0004 M nickel complex, 0.0002 M copper complex, and 0.0004 M cobalt complex in alcoholic solution were prepared by dissolving the calculated amounts of complex in absolute ethyl alcohol. Optical densities (D) were measured at

wave lengths between 400 and 800 μ with a model DU Beckman spectrophotometer, utilizing a 1 cm corex cell. The optical densities are plotted versus wave lengths in Fig. 1.

E. Electro Chemical Studies.*

1. Polarography.

To a 100 ml. volumetric flask were added 5 ml. of 1 M lithium chloride solution as the supporting electrolyte, 1 ml. of 1% gelatin solution, 5 ml. of 0.01 M of the solution to be studied, and 50 ml. of absolute ethyl alcohol. The solution was diluted to the mark with distilled water. A portion of this solution was then transferred to an H-type electrolytic cell, and nitrogen was bubbled through it for 30 minutes to remove the dissolved oxygen.

One side of the electrolytic cell was inserted under the dropping mercury electrode assembly until the capillary tip was completely immersed in the solution. The other side of the cell was connected to an external calomel reference electrode through a salt bridge containing one molar lithium chloride as the electrolyte.

Current voltage changes were recorded manually between 0 and -1.9 volts (versus the S. C. E.) in 0.01 volt increments, using the Sargent Manual Polarograph Model III.

* The author is indebted to Dr. Paul Delahay and to Mr. George Stiehl for valuable aid during the course of these investigations.

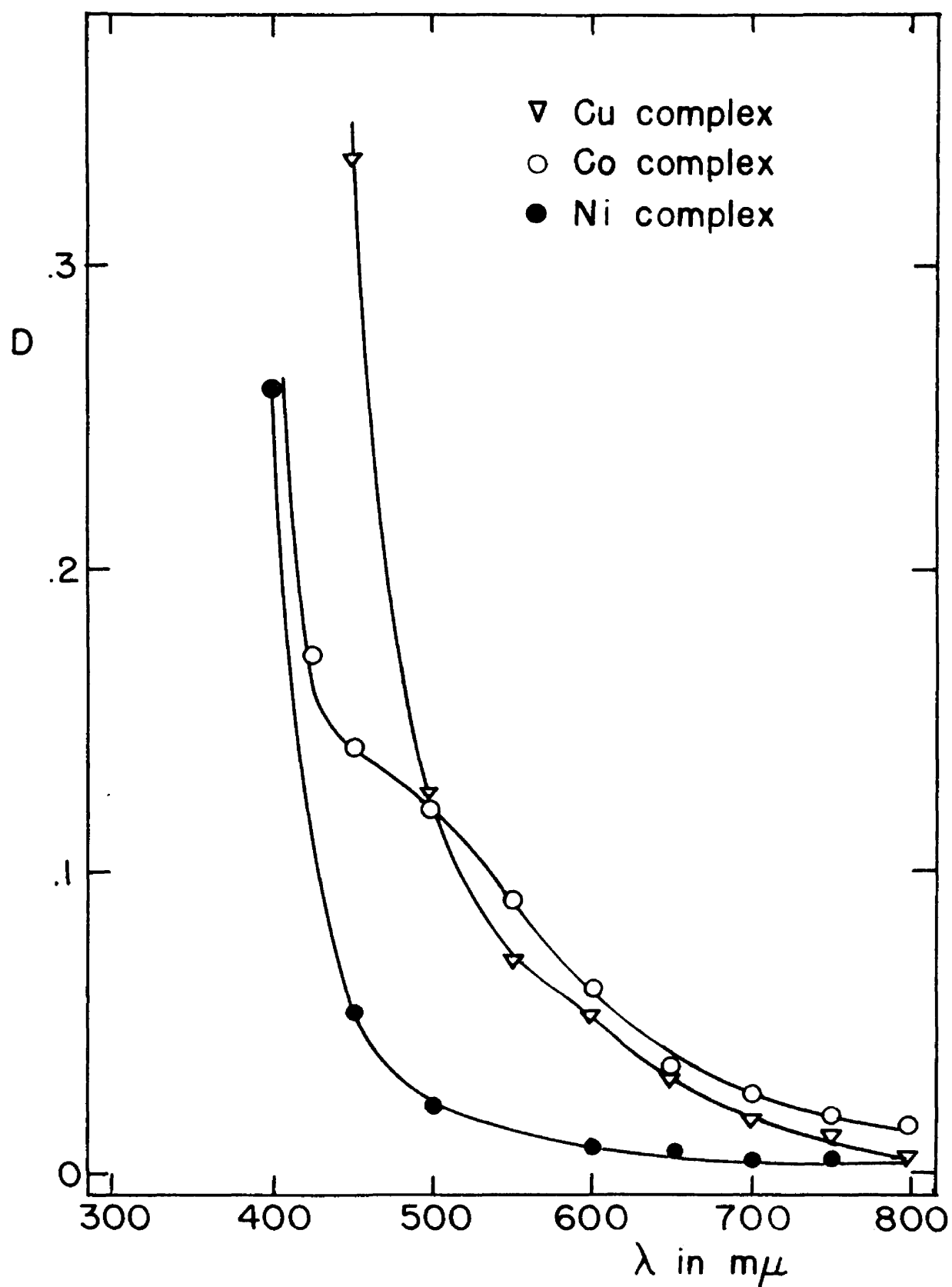


Figure. 1. Absorption Spectra of Copper, Cobalt, and Nickel Complexes.

The polarograms of mono-ortho-amino-benzaldehyde, tris-anhydro-ortho-amino-benzaldehyde, and the copper and nickel complexes of tris-anhydro-ortho-amino-benzaldehyde were obtained by this method; they have been plotted in Fig. 2 and 3.

2. Coulometry.

In order to obtain confirmatory evidence for the apparent oxidation states of the metals in the coordination compounds, recourse was taken to controlled potential electrolysis. The set-up used was similar to that described by Lingane (24), but modified by separating the reference electrode from the cell by means of an agar-lithium sulfate bridge. This bridge was surrounded by a concentric tube of larger diameter drawn out to a capillary at the end approaching the mercury cathode. The purpose of the bridge was to prevent diffusion of chloride ions from the reference electrode into the cell, for reasons evident from the experiments in Section I. (See the diagram in Fig. 4.)

When the electrolysis apparatus had been assembled, mercury was introduced into the cell until the platinum wire cathodic lead was completely covered by it. Thereupon 100 ml. of solution, 5×10^{-4} M in the complex to be analyzed and 5×10^{-2} M in lithium sulfate was placed in the cell on top of the mercury. Nitrogen was then bubbled through the solution for 30 minutes to remove the dissolved

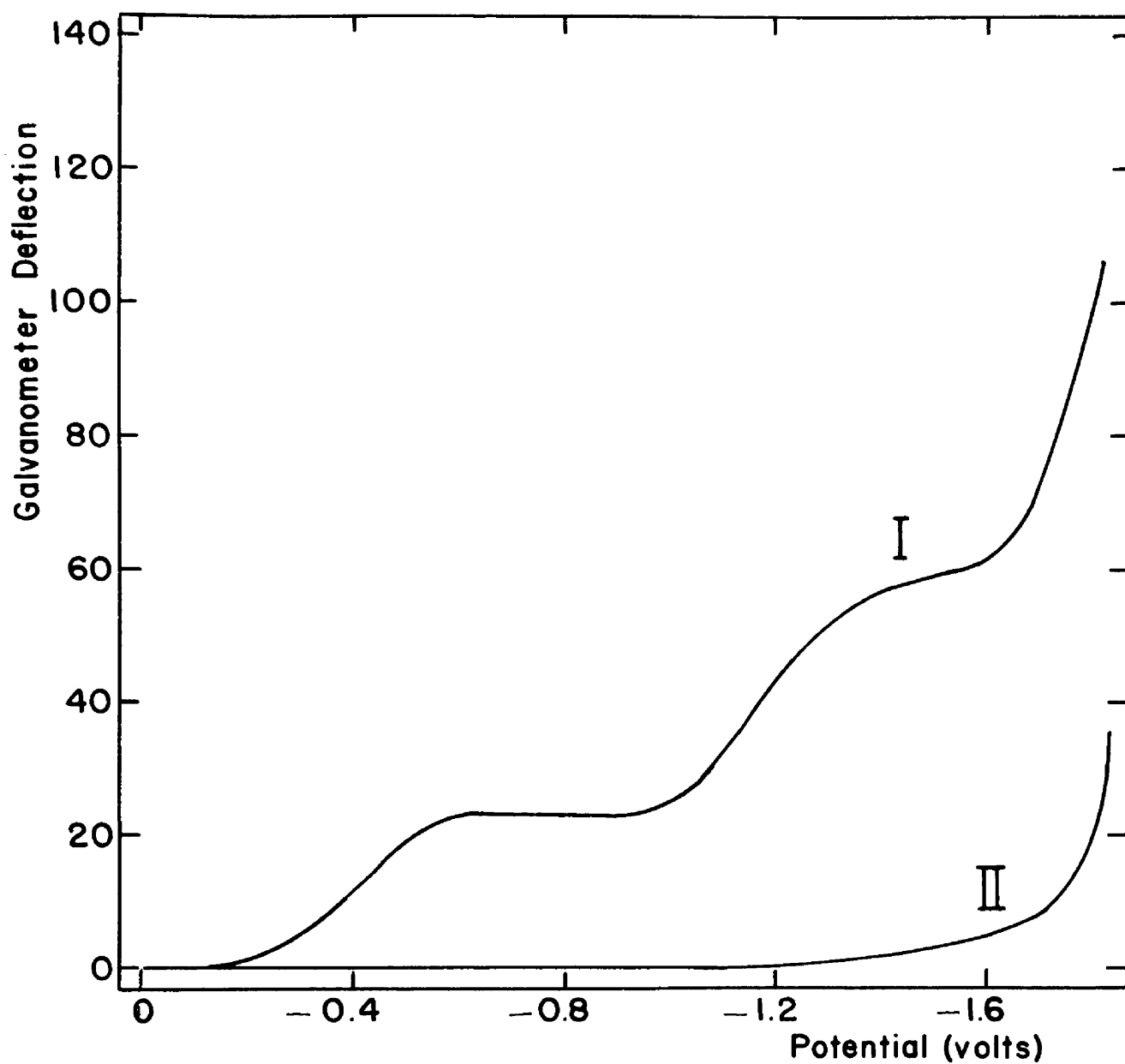


Figure 2. Polarograms of Tris-anhydro-ortho-aminobenzaldehyde (I) and Mono-ortho-aminobenzaldehyde (II).

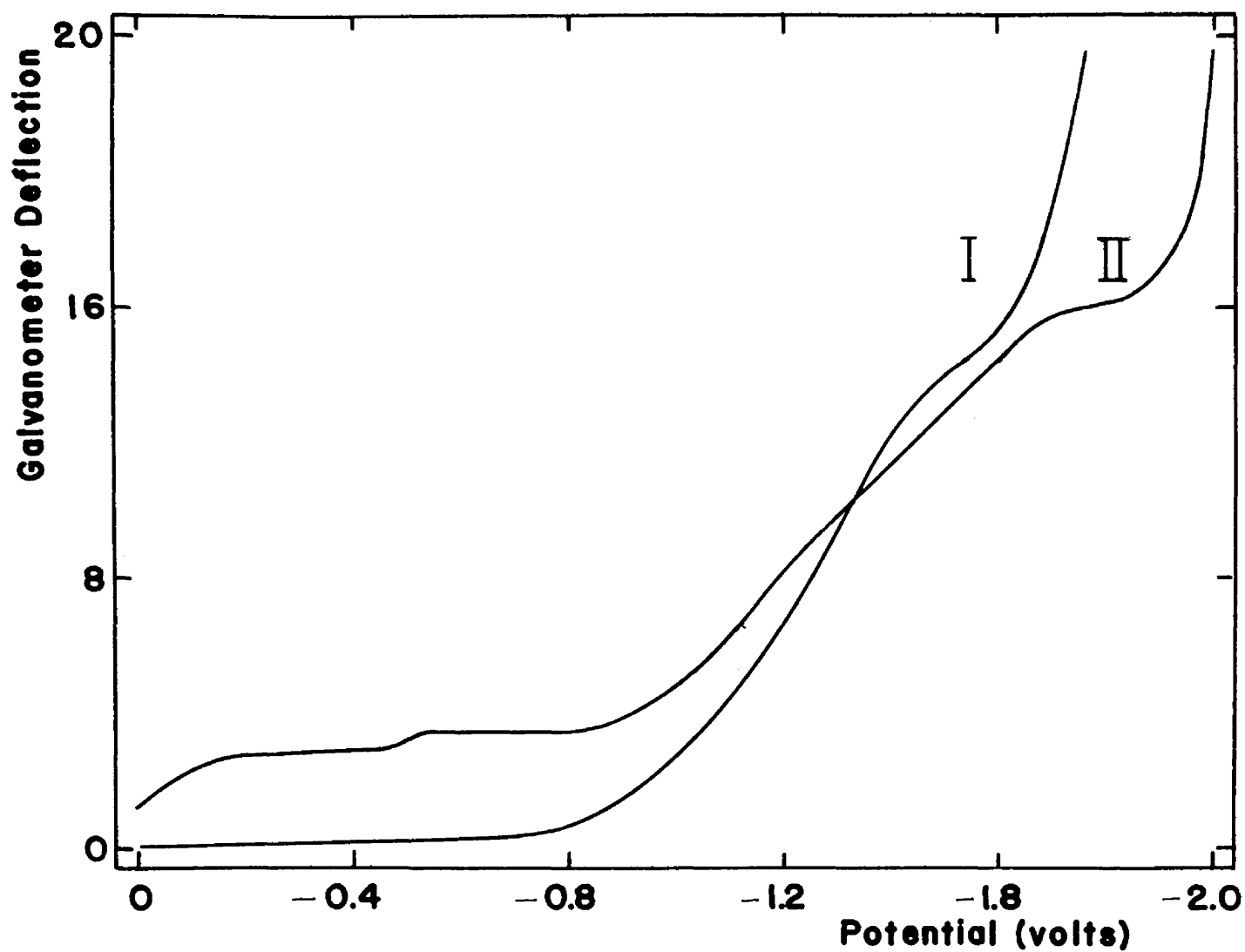


Figure 3. Polarograms of Copper and Nickel Complexes of Tris-anhydro-ortho-aminobenzaldehyde.

I. Nickel Complex.

II. Copper Complex.

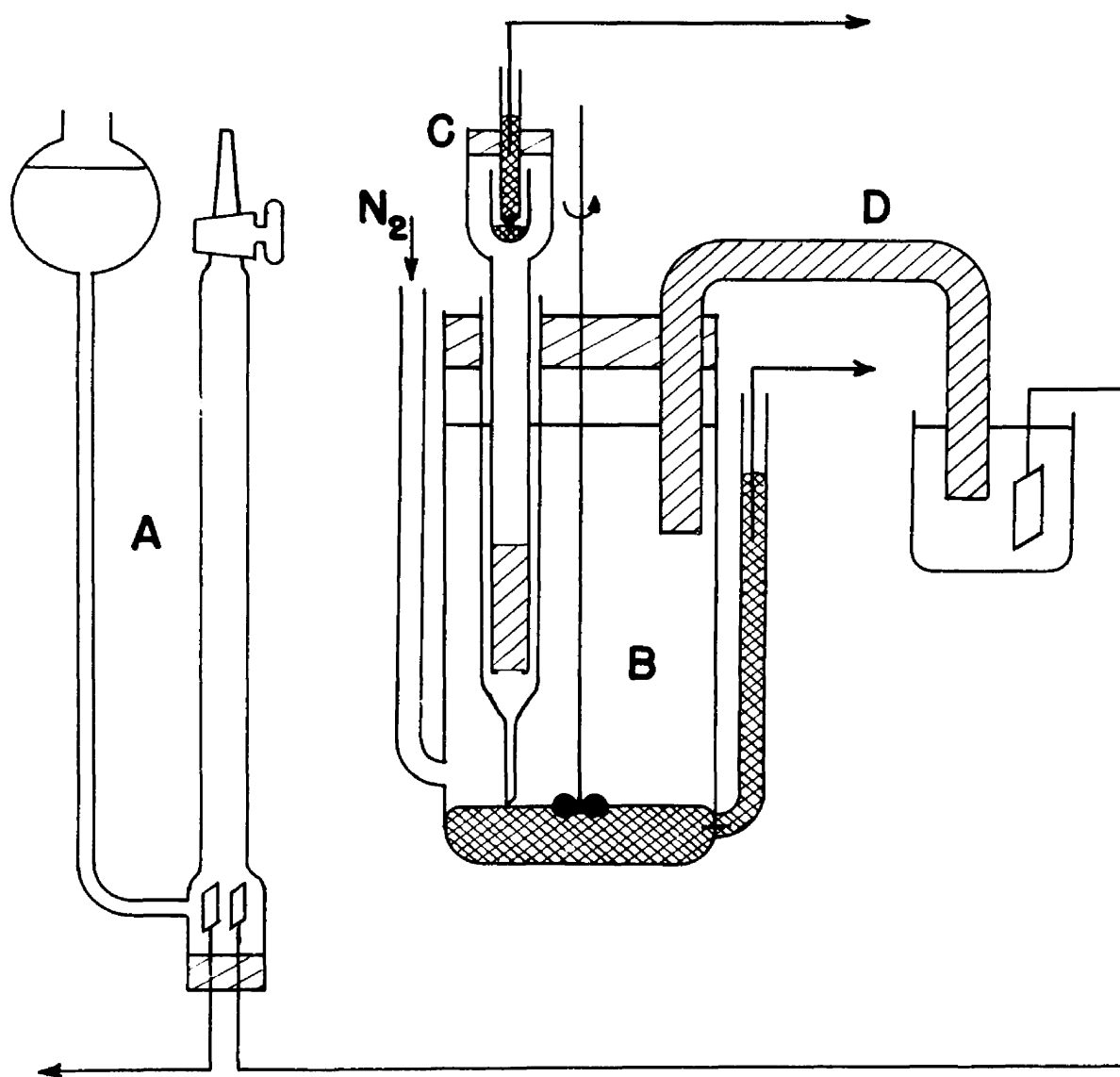


Figure 4. Apparatus Used for Coulometric Determination.

- (A) Gas Coulometer.
- (B) Electrolysis Cell.
- (C) Reference Electrode.
- (D) Salt Bridge.

oxygen. The stirrer was started, and the tip of the bridge from the reference electrode was adjusted so that it just touched the mercury surface. The gas coulometer was filled with 0.5 M potassium sulfate solution, which had been previously saturated with an oxygen-hydrogen gas mixture. The coulometer was connected to the cell, a potential difference applied and adjusted until the potential of the mercury cathode reached the value at which the operation was to be carried out. The electrolysis was discontinued when the current became negligibly small, and the volume of the oxygen-hydrogen mixture was recorded, after the solution remaining in the coulometer had been leveled with that in the bulb.

The apparatus and technique were checked by electrolyzing a solution of copper sulfate at a cathode potential of -0.5 volts. The volume of gas mixture, corrected for temperature and pressure, was in agreement with the theoretical value.

The electrolysis of the copper and nickel complexes was then carried out at a cathodic potential of -1.78 volts. The operation was concluded after four hours, when the current had dropped to about 0.01 milliampere, and negligible quantities of mixed gases were evolving in the coulometer. The results are gathered in table 2.

Table 2

Solution	Applied Pot. in Volts	Volume of Mixed H ₂ -O ₂ Gases in ml. at S. T. P.		No. of Electrons Reduced
		<u>Theoretical</u>	<u>Found</u>	
100 ml. of 5 x 10 ⁻⁴ M CuSO ₄	-0.5	1.68	1.51	2
100 ml. of 5 x 10 ⁻⁴ M Cu-Complex	-1.78	4.20	4.05, 4.01	5
100 ml. of 5 x 10 ⁻⁴ M Ni-Complex	-1.78	5.04	4.82, 4.80	6

F. Effect of pH on Copper Complex.

A variety of experiments demonstrated that the copper complex is stable toward acids, but undergoes a number of changes upon the addition of base.

When a dilute solution (0.00001 M) of the copper complex is treated with either sodium or ammonium hydroxide, the yellow color is immediately converted to orange-red. Immediate addition of acid to this orange-red solution brings back the original yellow color. If, however, the basic orange-red solution is permitted to stand in contact with the atmosphere, the color gradually fades, until, after two hours, the solution has become completely colorless. Addition of acid to this colorless solution produces no visible effect.

The change with pH in the absorption of 1.5×10^{-4} M complex solutions, that have been allowed to stand for 30 minutes, are recorded in Figure 5. The solutions ranged in pH from 2.6 to 8.8; the pH was adjusted with standard solutions of sodium hydroxide and hydrochloric acid. Since the basic solutions absorbed CO_2 , the recorded pH values were averages obtained from readings before and after the absorption measurements. Optical densities were read from the Beckman model DU spectrophotometer in 1 cm. corex cells.

When a concentrated (0.001 M) solution of the copper complex was treated with base, a brown precipitate, stable in air, was produced. This precipitate could be dissolved by the addition of acid, yielding a solution exhibiting the color characteristic of the original complex.

Acidification of solutions of the complex has no visible effect.

G. Displacement Reactions.

Two experiments were devised to determine the extent to which these complexes will exchange their metal ions.

In one experiment, 10 ml. of a 0.001 M copper complex solution were mixed with 10 ml. of a 0.001 M nickel complex solution, and allowed to remain standing for ten hours. Fig. 6. represents a comparison of the absorption spectrum of this solution with the spectra of the .001 M copper and nickel complexes.

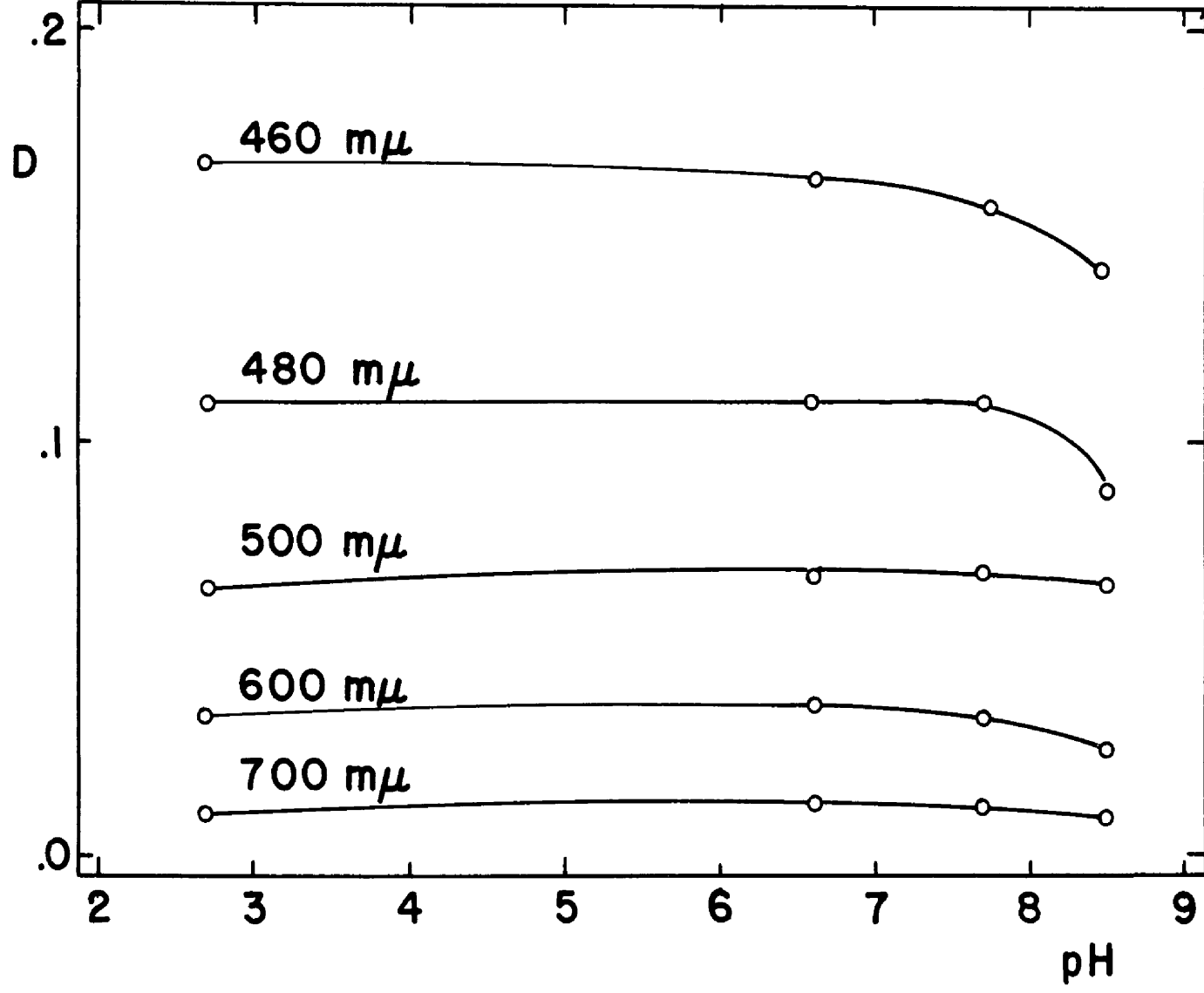


Figure 5. Variation of Optical Density (D) with Changes in pH of Copper Complex.

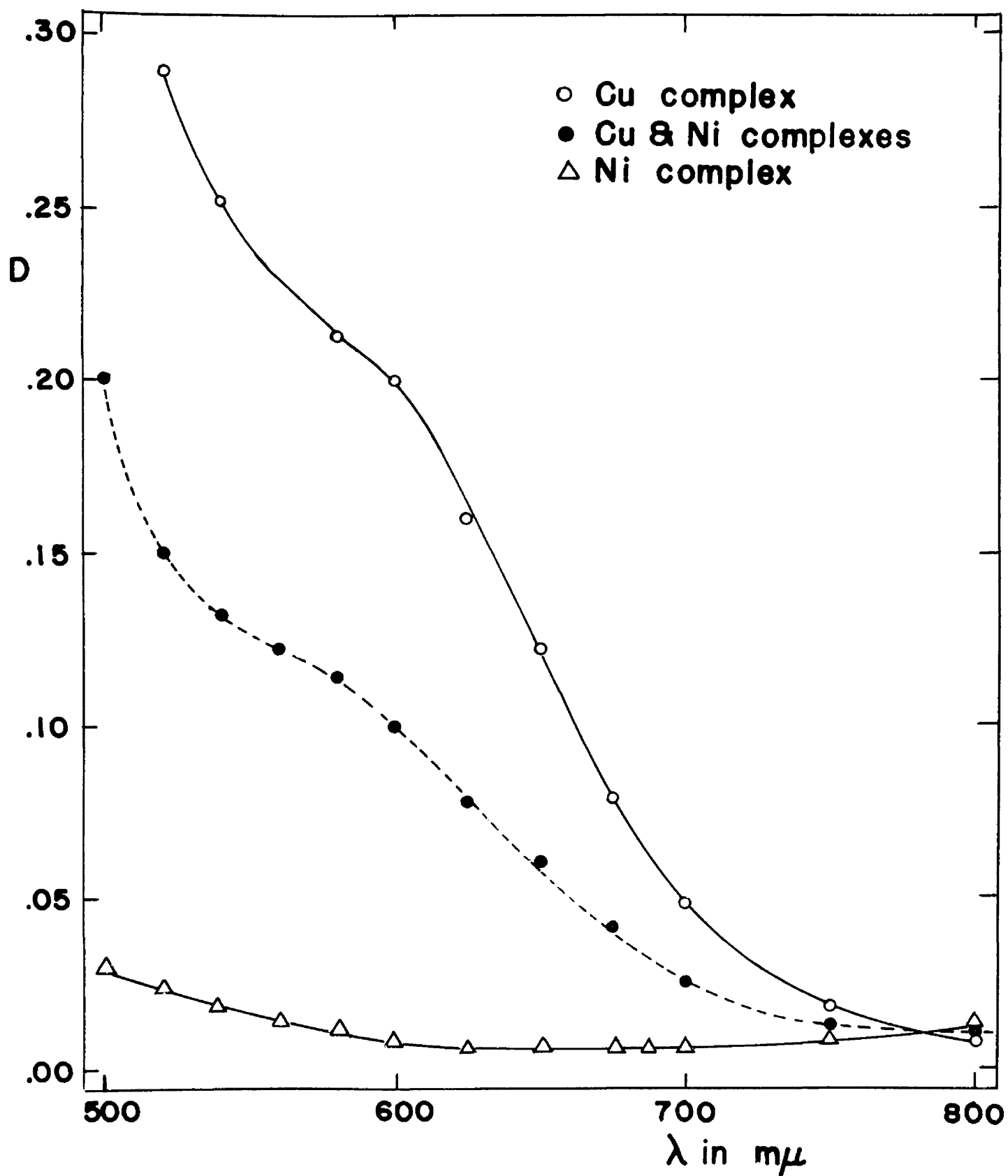


Figure 6. Absorption Spectra of Copper and Nickel Complexes and their Mixture.

Thereupon solutions were prepared from 10 ml. of 0.001 M copper complex and 10 ml. 0.001 nickel (II) nitrate, respectively. The absorption spectra of these solutions were also obtained after 10 hours, and plotted in Fig. 7.

H. The Reaction of Ethylenediamine with Tris-anhydro-ortho-aminobenzaldehyde and with its Metal Complexes.

The apparatus described for the preparation of the complexes was also employed in the following experiments.

1. Reaction between Tris-anhydro-ortho-aminobenzaldehyde and Ethylenediamine.

To 0.5 grams of the aldehyde trimer dissolved in 150 ml. of ethyl alcohol were added 1.6 ml. of 1 molar ethylenediamine. No precipitation had occurred after four hours of reflux, but the addition of water to the cooled solution resulted in the formation of a yellow solid, whose melting point and solubility characteristics were identical with those of the tris-anhydro-ortho-aminobenzaldehyde.

2. Reactions between the Cobalt Complex and Ethylenediamine.

To 0.5 grams of the cobalt complex in 150 ml. of alcohol were added 1.6 ml. of 1 M ethylenediamine in alcohol, and the mixture was refluxed for four hours. Addition of water to the cooled solution caused the formation of a brown precipitate, which melted at 110-112°C.

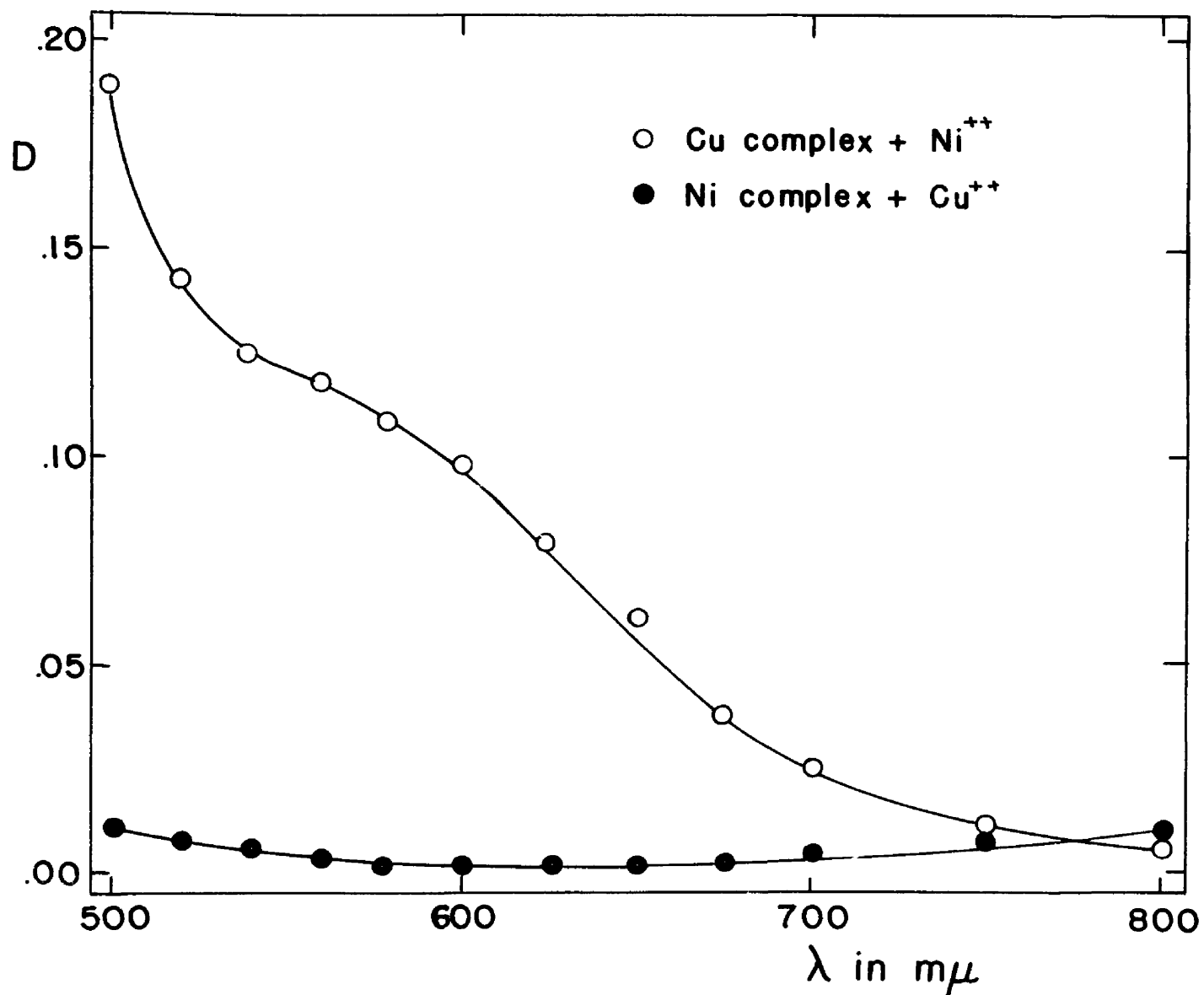


Figure 7. Absorption Spectra of Mixtures of Copper and Nickel Complexes with their Metal Salts.

Anal.: C, 73.96; H, 6.59; N, 10.41.

3. Reaction between the Nickel Complex and Ethylene-diamine.

0.5 grams of the nickel complex dissolved in 150 ml. of water was treated with 1.6 ml. of 1 M ethylene diamine in water. A red brown precipitate was formed. The mixture was digested for two hours, washed with water, and dried. M. P. 250-255°C. This precipitate was insoluble in water, but soluble in alcohol and acetone.

Anal.: C, 68.86; H, 5.21; N, 11.62.

4. Reaction between the Copper Complex and Ethylene-diamine.

On mixing 0.5 grams of the copper complex in 150 ml. of water with 1.6 ml. of 1 M ethylene diamine, a brown precipitate was formed, which turned light green after digestion for two hours. The melting point of the dried precipitate was found to be 155-158°C. This precipitate was insoluble in water but soluble in alcohol and acetone.

I. Reaction of the Copper Complex with Halide Ion and Metallic Mercury.

It was discovered during the preparation of the solution of copper complex for electrolysis that the surface of the mercury became coated with a blue crystalline material.

Experiments were then carried out to determine what conditions are required for the formation of the blue solid.

0.001 M solutions of the copper complex, added to a beaker whose bottom was covered with metallic mercury, were treated with solutions of lithium chloride, potassium bromide, potassium iodide, potassium sulfate, and potassium nitrate. It was found that the halide ions caused the formation of the blue crystals, whereas no changes occurred upon the addition of sulfate or nitrate.

Treatment of solutions of the copper complex with halide ion in the absence of metallic mercury produced no visible reaction. No reaction occurred also when the nickel complex was subjected to the conditions that produced the blue solid from the copper complex.

J. Attempted Trimerization of Ortho-aminobenzaldehyde in the Absence of Metal Ions.

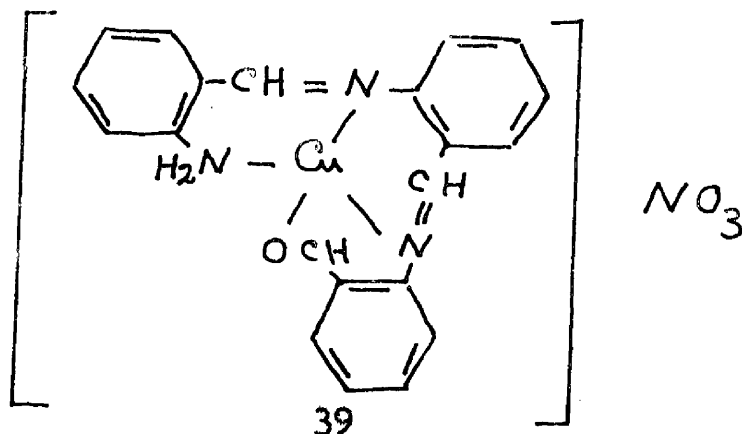
A solution of the monomeric aldehyde in alcohol was subjected to the same conditions that caused the formation of the trimer in the presence of metal ions; the latter were, however, omitted in this experiment. The addition of water to the reaction product did not yield any precipitate, indicating that no trimerization had taken place.

IV. DISCUSSION

A. The Catalytic Trimerization of Ortho-aminobenzaldehyde.

The evidence that has been summarized in the experimental section indicates that ortho-aminobenzaldehyde is subject to the same type of condensation in the presence of metal ions as the tetramerization of phthalonitrile to phthalocyanine. The two processes differ in that the latter does not take place in the absence of metal ions, whereas the former, though greatly accelerated by metal catalysis, does occur to some extent under non-complexing conditions.

The great difference in physical properties of the trimer discovered in this investigation and the trimer that has been reported in the literature leaves little doubt that two different compounds are involved. Although the experimental evidence for distinguishing between structures I and II in the metal complexes (pp. 14 and 15) is lacking, a comparison of the reaction investigated here with other complex forming reactions leads to the conclusion that the following configuration is probably involved:



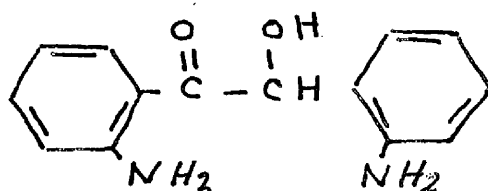
The structures of the nickel and cobalt complexes may be formulated in analogous fashion, with two nitrate ions serving to neutralize the charge of the cationic complex.

It is to be expected that the zinc chloride addition product of the compound obtained by Seidel has a structure similar to the metallic complexes discovered in the present investigation. It is possible that during the repeated recrystallizations from acetic acid, as a result of which the zinc was eliminated from the complex, the organic molecule was subjected to rearrangement to structure I. (p.14)

Conclusive proof for the trimeric nature of the condensation product is provided by the analysis of the product of the reaction of the monomer with manganese nitrate; the empirical formula of the compound was determined as $C_{21} H_{17} N_3 O$. Analyses of the copper, nickel, and cobalt complexes also lead to a formulation involving the quadridentate coordinating agent. The reaction with manganese ion undoubtedly proceeds through a complex intermediate, which, however, is considerably less stable than the corresponding complexes of the other metals, and consequently decomposes to yield the coordinating agent as the isolated product.

The catalytic behavior of metal ions in this reaction is further demonstrated by the failure of the ortho-amino-benzaldehyde to trimerize under conditions identical with those of the complexing reactions, but differing only in the absence of metal ion (p. 38).

It is of interest to note that when the aldehyde group of monomeric ortho-aminobenzaldehyde is blocked prior to reaction with a metal ion, no trimerization occurs. Such blocking can be achieved through reaction with ammonia or ethylenediamine (p. 16). Our experiments have shown that treatment of the trimer complexes with ethylenediamine does not result in the formation of the ortho-amino-benzal-ethylenediamine complexes, although it does promote the decomposition of the complex. Analysis of the product of the reaction of the cobalt complex with ethylenediamine (p. 35) yields values that conform to the composition of monomeric ortho-aminobenzaldehyde, although the melting point of the former is considerably higher than that of the latter. A possible explanation of these results is that a benzoin condensation has occurred; such a compound would have the following structure,



and would have an empirical composition identical with that of the uncondensed aldehyde.

B. The Stabilization of Low Oxidation States by Tris-anhydro-ortho-aminobenzaldehyde.

Analysis of the copper, cobalt, and nickel complexes showed that the copper complex held one nitrate ion per mole, whereas the nickel and cobalt complexes required two nitrate ions each for charge neutralization. Evidently the oxidation state of copper in the complex is +1, and the oxidation state of the other two ions is +2.

Confirmatory evidence for the existence of the metals in these oxidation states was furnished by the controlled potential electrolysis experiments. It was not possible to carry out the reduction of the ions without simultaneous reduction of the coordinating agent. Since the latter required four electrons for reduction, the oxidation state of the metal can be deduced by subtracting four from the total number of electrons utilized in the reduction of the complex. By this method the +1 state for copper and the +2 state for nickel were substantiated.

Tris-anhydro-ortho-aminobenzaldehyde apparently stabilizes the low oxidation states of metal ions. Cobalt, which frequently undergoes oxidation during complex formation, in this case remains in the +2 state. It is even more striking that copper, added to the reaction mixture as copper (II) nitrate, is reduced as a result of the coordination reaction.

The change in color from yellow to orange red of a dilute solution of the complex upon treatment with base (p. 31) may be explained in one of three ways:

1) hydroxide ion replaces some of the ligands of the coordinating agent, 2) the coordinating agent itself is modified, or 3) OH^- ion causes oxidation of the copper (I) to copper (II). Other observations eliminate all but the third possibility. The fading of the orange-red solution to colorless upon prolonged standing indicates that the copper (II) complex is relatively colorless, and that the orange-red is due to the presence of copper in two oxidation states simultaneously, a factor that generally gives rise to intense color. As long as any copper (I) remains in solution, it reforms the yellow acid solution upon reduction of pH, but if the copper (I) is permitted to remain in basic solution long enough to convert all of the copper to the +2 state, treatment with acid no longer has any effect. It should be noted that basic solutions generally stabilize the higher oxidation states of metal ions.

Addition of excess hydroxide to a concentrated solution of the copper complex (p. 32) causes immediate precipitation of a brown solid, which is probably the hydroxide of the copper (I) complex ion. The precipitated copper (I) complex is not subject to conversion to the +2 state, and therefore reforms the soluble copper (I) complex upon the addition of acid.

It can be concluded from an examination of Figure 7 that no exchange takes place between the nickel complex and copper (II) or between the copper (I) complex and nickel (II). Figure 6 reveals that the copper and nickel complexes, when present together in solution, have no effect upon each other, and do not enter into any exchange. These studies can be interpreted in one of two ways: 1) attainment of equilibrium is immeasurably slow, or 2) the copper (I) complex is much more stable than the nickel (II) complex, which in turn is considerably more stable than the copper (II) complex. The second alternative is by far the more plausible explanation, since the equilibrium that always exists between a complex and its dissociation products generally is conducive to rapid attainment of equilibrium between complexes in solution.

The formation of a blue crystalline solid by the addition of halide to a solution of the copper complex in contact with mercury (p. 37) can be explained in terms of a disproportionation of copper (I) to copper (0) and copper (II). The reaction is caused to come to completion through a combination of two factors: 1) the production of copper amalgam, and 2) the insolubility of the halide of the bivalent copper complex ion. The reduction to the 0 state is suggested by the requirement that the reaction must occur on a mercury surface. The blue color indicates copper (II); furthermore, the nickel complex does not yield to the reaction,

as indeed it should not, since nickel cannot be oxidized beyond the +2 state, except in very unusual circumstances.

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VITA

The author was born in Ana, Iraq on April 15, 1922. At the age of four he moved with his family to Baghdad, where he established his permanent residence. After completing his primary and secondary education he attended the Higher Teachers College of Baghdad in 1939. Four years later he received his Bachelor's Degree in Science. Immediately upon graduation he was appointed to a full time teaching assistantship in the department of chemistry of the Higher Teachers College. After four years of teaching, he was sent to the United States as a government student to study chemistry. In May, 1947, he arrived at the University of Texas, where he enrolled in the graduate school. In August, 1949, he received his Master's Degree in Chemistry. After spending two semesters at the University of Texas, he transferred to Louisiana State University in September, 1950. Since that time he has been working toward the Ph.D. Degree in Chemistry. In his last year at Louisiana State University, he was appointed to a graduate teaching assistantship in chemistry.

The author is a member of the American Chemical Society and Sigma Xi.

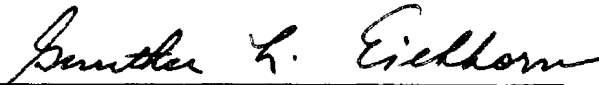
EXAMINATION AND THESIS REPORT

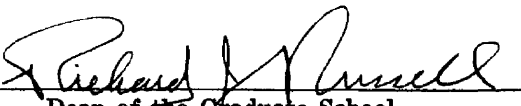
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Major Field: Chemistry

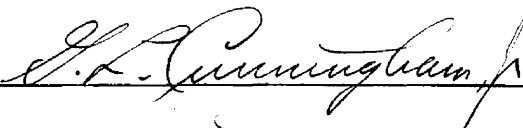
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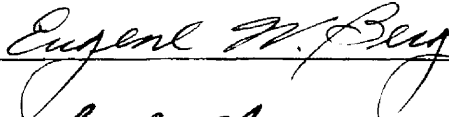


Major Professor and Chairman


Dean of the Graduate School

EXAMINING COMMITTEE:





Date of Examination:

February 20, 1953